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On the calculation of Mössbauer isomer shift

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A quantum chemical computational scheme for the calculation of isomer shift in Mössbauer spectroscopy is suggested. Within the described scheme, the isomer shift is treated as a derivative of the total electronic energy with respect to the radius of a finite nucleus. The explicit use of a finite nucleus model in the calculations enables one to incorporate straightforwardly the effects of relativity and electron correlation. The results of benchmark calculations carried out for several iron complexes as well as for a number of atoms and atomic ions are presented and compared with the available experimental and theoretical data. © 2007 American Institute of Physics.

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I. INTRODUCTION

In chemistry and solid state physics, Mössbauer spectroscopy¹ is commonly used as an analytic tool that provides a valuable information on the electronic structure of chemical compounds.^{2–9} The most well-known application of Mössbauer spectroscopy is the determination of iron ⁵⁷Fe in (crystalline or noncrystalline) solid samples. Besides ⁵⁷Fe the Mössbauer effect¹ is observed for more than 40 other elements in the Periodic Table, including elements such as tin, gold, mercury, etc.^{2–5} Mössbauer spectroscopy finds, therefore, a large and increasing number of applications not only in biological chemistry^{7,8} but also in nanoscience,⁹ materials science,⁴ metallurgy,^{10,11} and in space exploration studies.¹²

Mössbauer spectroscopy is based on the phenomenon of recoilless resonance absorption of γ rays by the atomic nuclei immersed in a (crystalline or disordered) solid medium.^{2–4} The frequency of the Mössbauer nuclear transitions is affected by the interaction with the surrounding electrons. This makes the primary parameters of Mössbauer spectra, such as the isomer shift, quadrupole splitting, and hyperfine splitting, sensitive characteristics of the electronic structure.^{2–4} However, the relationship of these parameters with the electronic structure is by no means straightforward.

It has been realized very early that the variation of the nuclear volume during the γ transition is responsible for the occurrence of Mössbauer isomer shift.¹³ Because an atomic nucleus is not a pointlike object but an object of a finite spatial extent (usually modeled by a sphere), the interaction energy between the nucleus and the external electronic density depends on the nuclear volume. This interaction alters slightly the frequency of the γ transition of a nucleus immersed in a specific electronic environment as compared to a bare nucleus. The isomer shift is defined as a measure of the energy difference between the energies of γ transitions occurring in the source nucleus and in the absorber nucleus.

Because the electronic environments in which the source and the absorber nuclei are immersed are different, the isomer shift probes this difference.^{2,3,14}

This simple model is expressed mathematically in Eq. (1).^{2,3,14}

$$\delta = \frac{c}{E_\gamma} \frac{4\pi}{5} ZS(Z)R^2 \left(\frac{\Delta R}{R} \right) (\bar{\rho}_e^a - \bar{\rho}_e^s), \quad (1)$$

where δ is the isomer shift measured in terms of the Doppler velocity necessary to achieve the resonance absorption, E_γ is the energy of the nuclear γ transition, c is the velocity of light, Z and R are the nuclear charge and radius, respectively, ΔR is the variation of the nuclear radius, and $\bar{\rho}_e^a$ and $\bar{\rho}_e^s$ are the average electronic densities inside the absorber and the source nucleus, respectively.

In theoretical models, the latter densities are commonly replaced with the nonrelativistically calculated electronic density at the nucleus.^{2,3,14} (Note that the pointlike nucleus model is conventionally employed in these calculations.) To introduce the effect of relativity and the effect of nonuniform electron density inside the nucleus, the $S(Z)$ factor is employed in Eq. (1).^{2,3,14–16} This factor is usually obtained from the comparison of the nonrelativistically calculated density at the nucleus (pointlike nucleus is employed) with the average density inside the nucleus obtained in relativistic atomic calculations, which employ a finite size nucleus.^{3,14–16} It was found that this factor is nearly constant for different states of the same atom. It was, therefore, suggested to scale the nonrelativistic electronic density with this factor in all compounds of the given element.^{3,14}

Theoretical calculations of the isomer shift focused primarily on the correlation between the electron density at the nucleus calculated with the use of molecular models and the observed values of the isomer shift for a series of chemical compounds of the given element.^{17–22} Indeed, because all the parameters in Eq. (1), with the exception of electron density, are constants for the given isotope, such a correlation seems

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sufficient for theoretical analysis of the experimental Mössbauer spectra. In this approach, the calibration constant α in Eq. (2),

$$\delta_i - \delta_j = \alpha(\rho_i(0) - \rho_j(0)), \quad (2)$$

is treated as an adjustable parameter and thus depends on the theoretical method employed for the calculation of the electron densities $\rho_i(0)$ at the nuclear position.^{17–22} The theoretical densities in Eqs. (1) and (2) can be obtained straightforwardly in the computational schemes based on the variational principle, such as the self-consistent field methods and Kohn-Sham density functional theory or the variational configuration interaction procedures. However, the application of perturbational methods, such as the many-body perturbation theory (MBPT), coupled cluster methods, and multireference extensions, requires the calculation of the so-called relaxed density matrix,²³ which correctly includes the orbital response into the density calculation. Presently, the relaxed density matrix calculations are not routinely available for multireference MBPT methods.²⁴

Besides the difficulties with obtaining correlated density in certain computational methods, the approach based on Eqs. (1) and (2) is inherently nonrelativistic.^{3,14} Indeed, when the pointlike nucleus model is employed, the density at the nucleus $\rho(0)$ remains finite only within the nonrelativistic framework. In the relativistic formalism, the density is divergent at the nucleus provided that a pointlike nucleus is employed.^{3,14} Therefore, the use of the $S(Z)$ factor remains the only way of introducing relativistic effects in Eq. (1). The numeric values of this factor were obtained from numeric atomic calculations.^{3,14–16}

It seems, therefore, desirable to go beyond Eq. (1) in the theoretical modeling of Mössbauer isomer shift and to develop a computational scheme that inherently incorporates electron correlation and relativistic effects. In the present article, a new computational approach is presented that is based on the explicit use of a finite nucleus model in connection with the relativistic formalism. The new method does not employ the electronic density explicitly and can be straightforwardly used with any correlated quantum chemical computational scheme. The underlying theory is presented in Sec. II. In Sec. III, the new scheme is applied to the calculation of the Mössbauer isomer shift for a number of atoms and for a series of iron complexes.

II. THEORY

The now standard approach to the theoretical description of Mössbauer isomer shift starts with many-electron problem in the Coulomb field of point nuclei.^{2,3,14} After this problem has been (approximately) solved, the effect of the finite nucleus volume is introduced as a perturbation. For simplicity, the nuclear charge distribution is taken as a uniformly charged sphere of radius R , where (following the concept of the “equivalent uniform distribution” introduced by Bodmer²⁵) R can be obtained from the experimental value of the root mean square (RMS) nuclear radius $\langle R^2 \rangle^{1/2}$, as in Eq. (3),²⁶

$$R = \sqrt{\frac{5}{3} \langle R^2 \rangle}^{1/2}. \quad (3)$$

The perturbation Hamiltonian (4) is the difference between the potential of the uniformly charged sphere and the usual Coulomb potential.^{2,3,14}

$$\Delta \hat{H}^{(\text{fr})} = \begin{cases} -(Z/2R)(3 - (r/R)^2) + Z/r, & r \leq R \\ 0, & r > R. \end{cases} \quad (4)$$

In Eq. (4), r is the distance from the center of the nucleus. Here for simplicity one nucleus is assumed; generalization to many nuclei is straightforward. In the first order of the perturbation theory, the expectation value of the perturbation Hamiltonian (4) yields the energy correction due to the finite nuclear volume. Assuming that the electron density inside the nucleus is constant,^{2,3,14} one arrives at Eq. (5),

$$\Delta E^{(\text{fn})} = \frac{2\pi}{5} Z R^2 \bar{\rho}_e. \quad (5)$$

Adding this energy correction to the ground and excited state levels of a bare nucleus (labeled with the 0 superscript), one obtains Eq. (6) for the energy of a Mössbauer transition of a nucleus immersed in the electronic environment,

$$E_\gamma^e = E_\gamma^0 + \frac{2\pi}{5} Z ((R + \Delta R)^2 - R^2) \bar{\rho}_e \approx E_\gamma^0 + \frac{4\pi}{5} Z R^2 \frac{\Delta R}{R} \bar{\rho}_e. \quad (6)$$

The approximation employed in Eq. (6) is justified by the small variation of nuclear radius upon excitation, which usually is of the order $\Delta R/R \approx 10^{-4}$.^{2,3,14} Equation (6) is straightforwardly converted to Eq. (1) by taking the difference between the energies of the resonance γ transitions for the absorber and for the source nuclei and converting it to a Doppler velocity necessary to achieve resonance absorption.

While Eq. (1) and argument leading to it are physically transparent, they are based on a number of simplifying assumptions, the most drastic of which is the assumption of the constant electron density inside the nucleus. This assumption is valid only for the nonrelativistic formalism, where $\bar{\rho}_e$ is replaced by the electron density at the nuclear position.³ Furthermore, it was assumed that the electron density is not dependent on the variation of the nuclear radius. To a certain degree of accuracy, relativistic effects can be reintroduced into Eq. (1) with the use of the scaling factor $S(Z)$, which can be obtained from the numeric atomic calculations carried out at the relativistic level.

From the underlying physical picture, it is apparent that the Mössbauer isomer shift has the same origin as the isotope shift of the electronic energy terms.²⁶ Indeed, the interaction with a nucleus of a finite volume results in the same energy shift of the electronic energy terms as for the nuclear terms. Therefore, assuming that the electronic system remains in the same eigenstate Ψ_e of the electronic Hamiltonian \hat{H}_e during the Mössbauer nuclear transition, the energy of the γ quantum can be written as in Eq. (7),

$$E_{\gamma}^e = E_{\gamma}^0 + \langle \Psi_e | \hat{H}_e(V_{Ne}^{(e.s.)}) | \Psi_e \rangle - \langle \Psi_e | \hat{H}_e(V_{Ne}^{(g.s.)}) | \Psi_e \rangle, \quad (7)$$

where $\hat{H}_e(V_{Ne}^{(g.s.)})$ is the electronic Hamiltonian, which depends on the electron-nuclear attraction potential $V_{Ne}^{(g.s.)}$. The latter is defined as the potential of a nucleus of a finite size. The superscripts (g.s.) and (e.s.) belong to the ground and the excited states of the nucleus, respectively. Assuming that the nucleus is spherically symmetric and keeping in mind that the variation of the nuclear radius is very small ($\Delta R/R \approx 10^{-4}$), one can write Eq. (8) for E_{γ}^e

$$E_{\gamma}^e = E_{\gamma}^0 + \left. \frac{\partial E_e(R_N)}{\partial R_N} \right|_{R_N=R} \Delta R + \frac{1}{2} \left. \frac{\partial^2 E_e(R_N)}{\partial R_N^2} \right|_{R_N=R} (\Delta R)^2 + \dots, \quad (8)$$

where $E_e(R_N)$ is the electronic energy calculated with the explicit account of the nucleus of a finite spatial extent characterized by the radius R_N . By convention, R_N is taken as the radius of the equivalent uniform distribution [see Eq. (3)].

Thus, the energy shift of the Mössbauer γ transition can be defined as the change in the electronic energy due to the variation of the nuclear radius. To the lowest order, only the first derivative can be kept in Eq. (8), which leads to Eq. (9) for the Mössbauer isomer shift,

$$\delta = \frac{c}{E_{\gamma}} \left(\left. \frac{\partial E_e^a(R_N)}{\partial R_N} \right|_{R_N=R} - \left. \frac{\partial E_e^s(R_N)}{\partial R_N} \right|_{R_N=R} \right) \Delta R. \quad (9)$$

In Eq. (9), E_e^a is the electronic energy of a system, which contains the absorber nucleus, and E_e^s is the electronic energy of a system, which contains the source nucleus.

Equation (9) as well as the standard Eq. (1) is based on a simplified model of the nucleus, which is treated as a uniformly charged sphere. However, the use of this model (as well as other nuclear models) leads to acceptably small error (estimated in Ref. 3 to be less than a few percent even for the heaviest elements) as long as the second moment of the nuclear charge distribution $\langle R^2 \rangle$ is reproduced correctly.³ Another potential source of error contained in Eq. (9) is due to the neglect of the higher derivatives of the electronic energy with respect to the nuclear radius. From the numeric examples given in the following section, it will be seen that these terms are extremely small and may be safely neglected.

Most straightforward a connection between Eq. (9) and the standard approach to Mössbauer isomer shift given in Eq. (1) can be established under the following assumptions: (i) the electronic energy is variationally obtained, (ii) the nuclear charge distribution is represented by a uniformly charged sphere, and (iii) the electron density inside the nucleus is represented by a constant. Under these assumptions one obtains Eq. (10) for the electronic energy derivative with respect to the nuclear radius,

$$\begin{aligned} \left. \frac{\partial E_e^a(R_N)}{\partial R_N} \right|_{R_N=R} &= \left\langle \Psi_e \left| \frac{\partial \hat{H}_e(V_{Ne})}{\partial R_N} \right| \Psi_e \right\rangle \bigg|_{R_N=R} \\ &= \left\langle \Psi_e \left| \sum_i \frac{3Z R_N^2 - r_i^2}{2 R_N^4} \right| \Psi_e \right\rangle \bigg|_{R_N=R} \\ &= \frac{4\pi}{5} Z R \bar{\rho}_e, \end{aligned} \quad (10)$$

where index i runs over all the electrons in the system and r_i is the distance between the center of the given nucleus and the i th electron. Substituting Eq. (10) into Eq. (9) one arrives at Eq. (1) (with the $S(Z)$ scaling factor omitted). Thus, under the above assumptions, Eq. (9) conforms with the standard theoretical approach to the Mössbauer isomer shift.^{2,3,14} It should be realized, however, that the assumptions (i)–(iii) do not restrict the applicability of Eq. (9) to methods based on the variational principle only. Equation (9) and the argument leading to it are based on the reciprocal character of the electron-nuclear interaction²⁶ and are valid even in connection with a nonvariational quantum chemical method, such as second order Møller-Plesset perturbation theory (MP2) or coupled cluster with single and double substitutions and non-iterative treatment of triple excitations [CCSD(T)], provided that a derivative of the electronic energy with respect to the nuclear radius can be obtained.

Employing the analogy between Eqs. (9) and (1), one can define the average density inside the nucleus, as in Eq. (11),

$$\bar{\rho}_e = \frac{5}{4\pi Z R} \left. \frac{\partial E_e^a(R_N)}{\partial R_N} \right|_{R_N=R}. \quad (11)$$

The so-defined density $\bar{\rho}_e$ can be used as an analog of the conventional density inside the nucleus and employed in connection with Eq. (1), instead of the density at the nuclear position traditionally employed in this equation. Note that, in this case, the relativistic scaling factor $S(Z)$ should be omitted in Eq. (1), because the relativistic corrections are already embedded into $\bar{\rho}_e$.

While, in theoretical models, a uniformly charged sphere is adopted as a model of a finite size nucleus,^{3,15,16,27} in practical quantum chemical calculations, another model based on the representation of the nuclear charge distribution by a Gaussian-type function is widely used.^{28,29} In this model, the parameter which defines the nuclear volume is the RMS nuclear radius $\langle R^2 \rangle^{1/2}$, and the nuclear charge density and the attraction potential due to the nucleus are given in Eqs. (12a) and (12b),²⁹

$$\rho_N(r) = \frac{Z}{\pi^{3/2}} \left(\frac{3}{2\langle R^2 \rangle} \right)^{3/2} - \exp\left(\frac{3}{2} \frac{r^2}{\langle R^2 \rangle} \right), \quad (12a)$$

$$V_N(r) = -\frac{Z}{r} \operatorname{erf}\left(\sqrt{\frac{3}{2}} \frac{r}{\langle R^2 \rangle^{1/2}} \right), \quad (12b)$$

where r is the distance from the center of the nucleus. Thus, in practical calculations with this model, it is convenient to express the quantities in Eqs. (9)–(11) in terms of the derivatives with respect to the RMS nuclear radius. Based on the

analysis presented in Ref. 3, the use of the Gaussian model should not lead to greater errors than the use of the uniformly charged sphere model, provided that the second moment $\langle R^2 \rangle$ of the nuclear charge distribution is accurately reproduced. It is well established that, even for elements as heavy as fermium ($Z=100$), the total electronic energies obtained with the use of the uniformly charged sphere nuclear model and with the Gaussian nuclear model differ by $\sim 10^{-3}$ percent.²⁹

The use of Eqs. (9)–(11) for the calculation of Mössbauer isomer shift has the advantage that relativistic and electron correlation effects can be conveniently included in the calculation. Indeed, the finite nucleus models are commonly used in the four-component relativistic calculations based on the Dirac Hamiltonian. The derivatives of the energy with respect to the nuclear radius (or RMS nuclear radius) can be done numerically, which enable one to employ even those computational schemes for which the relaxed density matrix is not available.

III. RESULTS AND DISCUSSION

The computational scheme based on Eqs.(9)–(11) was implemented in the COLOGNE2005 suite of programs.³⁰ The effect of relativity was included into atomic and molecular calculations with the use of the normalized elimination of the small component (NESC) method,³¹ which was implemented according to Ref. 32. The relativistic calculations have been carried out within the one-electron approximation.³³ The Gaussian nucleus model was employed in the calculations with the RMS nuclear radii taken from Ref. 29. For the sake of comparison, the nonrelativistic results were obtained with the same code by setting the velocity of light to 10^8 au (atomic unit). The atomic and molecular calculations have been carried out at the Hartree-Fock (HF)³⁴ level, at the MP2, and at the CCSD(T) (Ref. 35) levels of theory. All electrons were correlated in the post-HF methods. The open-shell systems were treated with the use of the spin-unrestricted formalism. On the atoms for which the isomer shifts were calculated the uncontracted basis sets specified below were employed. For other elements, the augmented correlation consistent double-zeta (aug-cc-pVDZ) basis sets of Dunning³⁶ were used. All basis sets, including aug-cc-pVDZ, were used in the uncontracted form.

First, let us test whether keeping only the first derivatives of energy with respect to the nuclear radius [see Eq. (9)] is an accurate approximation. Figure 1 shows the dependence of the total electronic energy of the tin atom calculated at the NESC/HF level of theory versus the RMS nuclear radius. The uncontracted (21s15p11d2f) basis set of Dyal³⁷ augmented with four tight *s*-type primitive functions was employed for tin. This plot shows that the dependence of the energy on the nuclear radius is nearly perfectly linear. Numerical analysis of the curvature of the electronic energy as a function of nuclear radius shows that the relative contribution of the second order term in Eq. (8) is of the order of 10^{-4} . Therefore, retaining only the linear term in Eq. (9) leads to a sufficiently good approximation. Thus, throughout

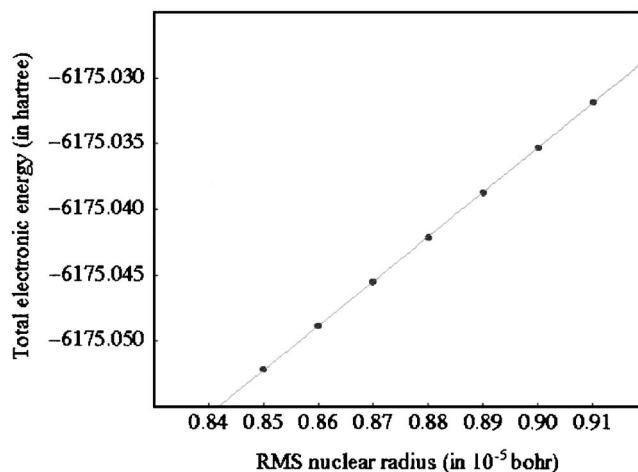


FIG. 1. Total electronic energy of Sn (in hartree a.u.) calculated at the NESC/HF level of theory as a function of the RMS nuclear radius (given in 10^{-5} bohr).

this work, the derivatives $\partial E_e^a(R_N)/\partial R_N$ were obtained numerically from the central differences with the increment of 10^{-6} bohr for the RMS nuclear radius.

In Table I, the results of relativistic and nonrelativistic atomic calculations of the average electron density inside the nucleus $\bar{\rho}_e$ according to Eq. (11) are presented. The calculations are carried out for the ground electronic states of iron and tin atoms. The uncontracted (20s12p9d) basis set for iron is taken from Ref. 38 and is augmented with four tight *s*-type primitive functions and with a set of polarization functions taken from the TZVPP basis set of Ahlrichs and May,³⁹ thus yielding a (24s13p9d1f) basis. The reference literature data in Table I were taken from the numeric atomic calculations carried out¹⁵ at the relativistic level, with the use of the $X\alpha$ method, and at the nonrelativistic level, with the use of the HF method.¹⁷ Note, however, that a finite nucleus model (uniformly charged sphere) was employed only in the $X\alpha$ calculations.¹⁵ The numeric HF reference datum is merely the density at the position of the pointlike nucleus. Notwithstanding the difference in the theoretical methods used in the present work and in the literature, the comparison of the HF results shows that the procedure suggested in Sec. II is capable of accurately reproducing the average densities $\bar{\rho}_e$ obtained within the standard approach [see Eq. (1)].

From Table I, it is seen that the inclusion of the electron correlation has relatively minor effect on the average densi-

TABLE I. Average density inside the nucleus $\bar{\rho}_e$ (in bohr⁻³) evaluated from Eq. (11) for the ground states of neutral iron and tin atoms. See text for detail on the basis sets employed.

	HF	MP2	CCSD(T)	Ref. data
Fe	14 894.186 (11 850.384) ^a	14 895.146 (11 850.861)	14 894.788 (11 848.838)	15 092.04 ^b (11 903.987) ^c
Sn	183 409.328 (86 922.221)	183 417.235 (86 923.559)	183 414.567 (86 922.479)	187 005.5 ^b ...

^aIn parentheses, the results of the nonrelativistic calculations obtained by setting the velocity of light to 10^8 AU.

^bNumeric relativistic X_α value from Ref. 15.

^cNumeric nonrelativistic HF value from Ref. 17.

TABLE II. Average density [Eq. (11)] inside the nucleus $\bar{\rho}_e$ (in bohr⁻³) and density differences for coinage metal atoms and singly charged ions. Total densities are given for neutral atoms and density differences ($\bar{\rho}_e^{\text{ion}} - \bar{\rho}_e^{\text{atom}}$) for ions. See text for detail on the basis sets employed.

		HF	MP2	CCSD(T)
Cu	$d^{10}s^1$	21 840.128 (16 531.808) ^a	21 840.374 (16 532.316)	21 840.898 (16 531.220)
	d^{10}	-4.965 (-3.480)	-12.230 (-6.418)	-9.975 (-4.739)
	d^9s^1	+5.166 (+3.935)	+5.769 (+2.780)	+6.101 (+3.943)
Ag	$d^{10}s^1$	140 612.013 (72 033.979)	140 618.306 (72 035.188)	140 617.171 (72 034.805)
	d^{10}	-13.390 (-5.537)	-17.205 (-7.279)	-16.126 (-7.015)
	d^9s^1	+12.077 (+6.021)	+10.254 (+5.271)	+10.606 (+5.356)
Au	$d^{10}s^1$	1 945 765.104 (345 555.328)	1 945 854.546 (345 554.822)	1 945 842.557 (345 554.031)
	d^{10}	-107.559 (-10.148)	-121.429 (-12.185)	-112.087 (-11.642)
	d^9s^1	+60.446 (+9.649)	+53.698 (+8.886)	+55.316 (+8.827)

^aIn parentheses, the results of the nonrelativistic calculations obtained by setting the velocity of light to 10⁸ AU.

ties $\bar{\rho}_e$ obtained with Eq. (11). This observation, however, does not hold for the density differences between different states of atoms. In Table II, the results of the calculations of the average density $\bar{\rho}_e$ for a series of coinage metal atoms are presented. The following basis sets are employed: the (24s13p9d1f) basis set for copper constructed in the same way as for iron, the (25s14p10d2f) basis set for silver obtained in the same way as for tin, and the (24s19p12d8f) basis set for gold obtained from the uncontracted (22s19p12d8f) basis set of Dyall³⁷ by augmenting it with two tight *s*-type primitive functions.

The calculations have been carried out for the ground

states of the neutral atoms and for the two states of singly charged ions in the configurations d^{10} and d^9s^1 . While for the neutral atoms the correlation effect on the total density $\bar{\rho}_e$ is small, it is more pronounced for the difference densities. The difference densities from the correlated and the uncorrelated calculations can differ by a factor of 2 and more. This dependence on the electron correlation is more pronounced for the lighter copper than for heavier silver and gold. For the latter atoms, relativistic effects prevail.

Importance of electron correlation for the distribution of the valence electrons is well established, see, e.g., pioneering works of Siegbahn and co-workers⁴⁰ on metal complexes. However, the importance of electron correlation for the densities of the core electrons in connection with Mössbauer isomer shift was not carefully investigated in the literature; although, there are studies of the effect of electron correlation on the nuclear quadrupole splitting parameters.⁴¹

Isomer shifts for iron compounds are calculated within the cluster approach. This approach is universally adopted in the quantum chemical calculations of Mössbauer parameters.^{3,17-22} Within the cluster approach, a solid is modeled by a suitably chosen cluster of the central atom, which contains the Mössbauer active nucleus, surrounded by a number of ligands. Although such an approach may be less accurate for the clusters with large negative charge, it has been shown that the effect of crystal environment on the calculated densities at the nucleus is small.¹⁷ Therefore this approach is employed in the present work for the purpose of better comparison with the results obtained within the standard approach.

The following clusters have been chosen in the present work as representatives of the respective solids: [FeF₆]³⁻ as a model of FeF₃,⁴² [FeBr₄]⁻ as a model of N(C₂H₅)₄FeBr₄,⁴³ [FeCl₄]⁻ as a model of N(C₂H₅)₄FeCl₄,⁴³ [Fe(CN)₆]³⁻ as a model of K₃Fe(CN)₆,⁴⁴ [FeO₄]²⁻ as a model of K₂FeO₄,⁴⁵ and [Fe(CN)₆]⁴⁻ as a model of K₄Fe(CN)₆.⁴⁴ The molecular geometries were taken from the compilation in Ref. 21.

Isomer shifts calculated with the use of the relativistic NESC/HF and NESC/MP2 methods as well as the nonrela-

TABLE III. Mössbauer isomer shifts (in mm/s) for a series of iron compounds calculated with the use of relativistic (NESC) and nonrelativistic methods. See text for detail on the basis sets employed. All shifts are given with respect to [Fe(CN)₆]⁴⁻. Experimental isomer shift of -0.02 mm/s from Ref. 44.

	HF		MP2		Expt.	Ref. ^b
	Rel.	Nonrel. ^a	Rel.	Nonrel.		
[FeF ₆] ³⁻	+0.27	+0.19	+0.41	+0.29	+0.50 ^c	+0.71; ^d +0.67 ^e
[FeBr ₄] ⁻	+0.09	-0.03	+0.32	+0.14	+0.29 ^f	+0.47; ^d +0.49 ^e
[FeCl ₄] ⁻	-0.02	-0.03	+0.18	+0.14	+0.22 ^g	+0.42; ^d +0.46 ^e
[Fe(CN) ₆] ³⁻	-0.22	-0.18	+0.05	+0.03	-0.11 ^h	0.0; ^d -0.22 ^e
[FeO ₄] ²⁻	-1.00	-0.78	-0.31	-0.29	-0.67 ⁱ	-0.72; ^d -0.96 ^e

^aNonrelativistic results are obtained by setting the velocity of light to 10⁸ AU.

^bReference literature data.

^cExperimental isomer shift of +0.48 mm/s from Ref. 42.

^dB3LYP isomer shifts (mm/s) from Ref. 21.

^eBPW91 isomer shifts (mm/s) from Ref. 22.

^fExperimental isomer shift of +0.27 mm/s from Ref. 43.

^gExperimental isomer shift of +0.20 mm/s from Ref. 43.

^hExperimental isomer shift of -0.13 mm/s from Ref. 44.

ⁱExperimental isomer shift of -0.69 mm/s from Ref. 45.

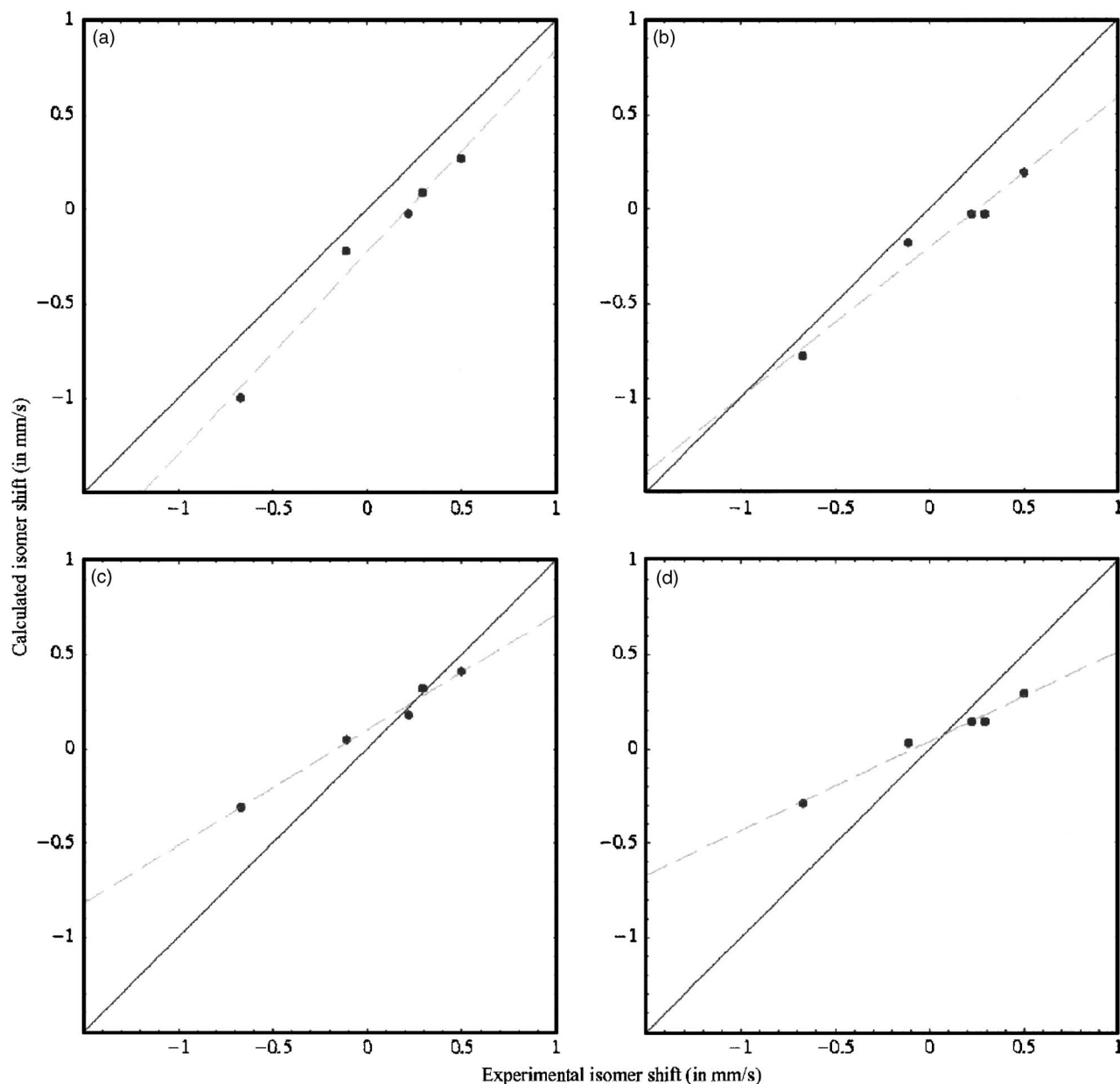


FIG. 2. Experimental vs calculated isomer shift (in mm/s) for a series of iron complexes reported in Table III: panel (a), NESC/HF; panel (b), nonrelativistic HF; panel (c), NESC/MP2; and, panel (d), nonrelativistic MP2. See Table III for numeric values of the isomer shifts. In each panel, solid line shows the ideal correlation between the theoretical results and the experiment, and dashed line shows actual linear least squares fit of the theoretical results (see text for more detail).

tivistically calculated values are reported in Table III and presented in graphic form in Fig. 2. The isomer shifts are given with respect to $[\text{Fe}(\text{CN})_6]^{4-}$ cluster model. This compound is chosen as a reference, because $\text{K}_4\text{Fe}(\text{CN})_6$ possesses the smallest (in absolute magnitude) isomer shift of all the compounds considered. When calculating the isomer shifts, the average densities inside the nucleus $\bar{\rho}_e$ were first calculated according to Eq. (11). Then, the relative isomer shifts were obtained according to Eq. (2) with the constant $\alpha = -0.1573a_0^3 \text{ mm s}^{-1}$, which was calculated from the experimentally obtained parameters of the ^{57}Fe nuclear transitions reported in Ref. 3.

The results in Table III and in Fig. 2 indicate that both relativistic and correlation effects are important for the accurate quantitative description of the Mössbauer isomer shift.

Indeed, the nonrelativistic HF values for $[\text{FeF}_6]^{3-}$, $[\text{FeCl}_4]^-$, and $[\text{FeBr}_4]^-$ are far too low. The latter two values have incorrect sign. The inclusion of the electron correlation, in the nonrelativistic MP2, makes these values more positive, however, at a price of deteriorating the calculated isomer shifts for $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{FeO}_4]^{2-}$. Note that the δ values for $[\text{FeCl}_4]^-$ and $[\text{FeBr}_4]^-$ remain indistinguishable at the nonrelativistic level of description.

The inclusion of relativistic effects, in the NESC/HF and NESC/MP2 calculations, helps us to improve the description of isomer shifts. However, at the HF level, the values of δ still remain too negative. The description improves at the NESC/MP2 level; however, for $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{FeO}_4]^{2-}$ the δ values become too positive. The MP2 method provides

only an approximate inclusion of the electron correlation, and it is expected that the use of a more sophisticated correlated method, such as CCSD(T), can bring a substantial improvement. Due to the size of the basis sets employed in this study, it was not possible to finish the CCSD(T) calculations for the iron compounds. However, from the results in Tables I and II, it may be expected that the results of the CCSD(T) calculations will be intermediate between the HF and the MP2 results, which implies improved agreement with the experiment.

From the least squares linear fit (dashed lines in Fig. 2) of the calculated isomer shifts, it is seen that the NESC/HF shows a systematic error yielding too negative values of δ . However, the slope of the linear fit is nearly perfect for NESC/HF (slope: 1.0693 and intercept: -0.2250). For the nonrelativistic HF method, the slope is 0.7927 and intercept is -0.2025 , which implies poorer correlation with the experimental data than for the relativistic HF method. The same trend—relativistic is better than nonrelativistic—is observed for the MP2 calculations. For the NESC/MP2 method, the slope and the intercept of the linear fit are 0.6119 and 0.1019, and for the nonrelativistic MP2, the slope and the intercept are 0.4720 and 0.0403, respectively. These observations illustrate the well-known fact that, even for elements as light as iron, the proper account of relativity is important for obtaining a good description of the Mössbauer spectroscopy parameters.^{16,18}

It is worthwhile to compare the results obtained in the present work with the results from the traditional approach available in the literature. In the last column of Table III, the relative isomer shifts obtained from the data reported in the literature^{21,22} are shown. Note that, within the traditional approach, the proportionality constant α in Eq. (2) is treated as an adjustable parameter.^{17–22} The values of this parameter were obtained in Refs. 21 and 22 by the least squares fit of the calculated electron densities at the nucleus versus the observed isomer shifts. With the use of this protocol, the value of α depends on the choice of the computational method. Thus, in Ref. 21, with the use of nonrelativistic B3LYP calculations, a value of $\alpha = -0.366\,62a_0^3\text{ mm s}^{-1}$ was obtained, which differs by a factor of 2 from the experimental estimate for this parameter. From the nonrelativistic BPW91 calculations with an uncontracted basis set, a value of $\alpha = -0.357a_0^3\text{ mm s}^{-1}$ was obtained in Ref. 22. In spite of the parameterization against the experimental data, the results from the traditional approach to the Mössbauer isomer shift do not appear to be more accurate than the results obtained in the present work. Note that no fitting against experimental data was employed in the present work. Therefore, with the use of the new method it is possible to achieve the same or better accuracy in the calculation of Mössbauer isomer shift, as within the traditional approach without the necessity to resort to any type of parameterization against experimental data. A more thorough comparison with the traditional approach to the Mössbauer isomer shift will be published elsewhere.

IV. CONCLUSIONS

A new quantum chemical approach to the calculation of Mössbauer isomer shift is suggested. In the new approach, the isomer shift δ is calculated as the derivative of the electronic energy with respect to the radius of a nucleus of a finite volume. While, in the present work, the Gaussian nucleus model is employed,^{28,29} the approach is applicable with any existing theoretical model of a finite size nucleus, which correctly reproduces the second moment of the nuclear charge distribution.

The new approach has the advantage that the effects of electron correlation and relativity can be straightforwardly incorporated in the calculations. The results of benchmark calculations carried out with the use of the relativistic formalism (the NESC method^{31,32}) and with the nonrelativistic approach strongly indicate the importance of including relativity even for light elements, such as iron. The importance of the proper account for electron correlation is evidenced by the results of the post-HF calculations for a series of iron compounds. Notwithstanding a relatively low level of treatment of the electron correlation (at the MP2 level), a considerable improvement of the quantitative agreement with the experiment is achieved for a number of compounds studied. Thus, the accurate description of the Mössbauer spectroscopy parameters requires the inclusion of both effects, relativity and electron correlation.

In the present work, a number of technical issues, such as the basis set dependence of the results, the applicability of density functional theory, the necessity of the inclusion of environmental effects, etc., were not addressed. These questions will be studied in the forthcoming publications. In view of the growing interest in Mössbauer spectroscopy for the study of biological systems and emerging new materials, especially in nanoscience,^{4–12} the new approach can become a useful tool for theoretical interpretation of the experimental data.

For the full theoretical characterization of Mössbauer spectra, the account of magnetic hyperfine splitting and of electrostatic quadrupole splitting is necessary. A promising approach to the calculation of hyperfine structure constants has been recently suggested by us.⁴⁶ Work on the improvement of this approach and on testing it against the relevant experimental data is currently in progress.⁴⁷

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